

The influence of catalyst acid strength on reactions relevant for Methanol To Hydrocarbons (MTH) catalysis

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Acid catalysis is important in many chemical reactions, not least in the petrochemical industry where acidic zeolite catalysts are used in major processes such as catalytic cracking. Fundamental understanding of the effect of Brønsted acid strength on key reactions is therefore a topic of major interest. Yet, few examples of such studies exist. In one of the few available studies of acid strength Macht et al. [1] recently suggested that reactions involving transition states with localized charges are less sensitive to changes in acid strength than those with diffuse charges.

This contribution compares two isostructural catalysts with different acid strength, H-SSZ-24 and H-SAPO-5 (AFI), for methanol to hydrocarbons (MTH) catalysis and key reaction steps relevant to this process. The MTH reaction is a flexible reaction route to produce light alkenes or gasoline from alternative hydrocarbon feedstocks such as natural gas, biomass or coal [2]. Under steady-state MTH conditions, direct reactions between methanol molecules are insignificant. Instead, product formation proceeds via continuous methylation of an adsorbed hydrocarbon pool, which subsequently eliminates alkenes. The complexity of the reaction means that key reaction steps might exhibit different sensitivities to a change in acid strength, and that overall selectivity may be tailored by changing the acid strength.

When the product selectivity in the MTH reaction was compared in the two materials employed here, it was found that the strongly acidic H-SSZ-24 is more selective towards aromatic products and light alkenes (C₂-C₃) than the moderately acidic H-SAPO-5 [3]. Furthermore, isotopic labelling studies implied that while aromatic hydrocarbon pool species appear to play an important role in H-SSZ-24, these are of less importance in the weaker acid H-SAPO-5 [3]. To elucidate the reasons for this change in the major reaction intermediates, an understanding of the key reaction steps involved in the MTH reaction and their individual sensitivity to changes in acid strength is necessary.

The current study focuses on methylation reactions in the two catalysts. Co-reactions and kinetic investigations strongly suggest that the methylation of alkenes is strongly favoured relative to methylation of aromatics in H-SAPO-5, while methylation of aromatics is facile over H-SSZ-24. Concurrently with the reactor studies, periodic DFT based simulations are used to investigate adsorption in the two catalysts. The key methylation reactions are also studied by means of a molecular dynamics approach, which provides insight in the reactivity of the different adsorption complexes and allows investigation of temperature effects [4].

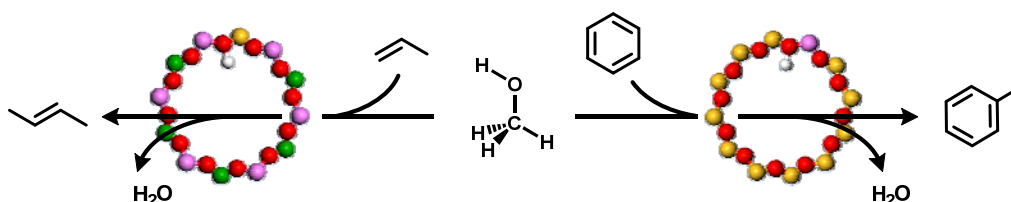


Figure 1. While the strongly acidic H-SSZ-24 prefers aromatic intermediates, methylation of alkenes is strongly preferred in the moderately acidic H-SAPO-5

References

- [1] J. Macht et al., *J. Am. Chem. Soc.*, 131 (2009) 6554.
- [2] U. Olsbye et al., *Angew. Chem., Int. Ed.*, 51 (2012) 5810.
- [3] M. Westgård Erichsen et al., *Catal. Today*, 215 (2013) 216
- [4] S.L.C. Moors et al., *ACS Catal.*, 3 (2013) 2556